

**DETECTION OF EVOLVED CARBON DIOXIDE IN THE ROCKNEST EOLIAN BEDFORM BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT AT THE MARS CURIOSITY LANDING SITE.** B. Sutter<sup>1</sup>, D. Archer<sup>2</sup>, A. McAdam<sup>3</sup>, H. Franz<sup>3</sup>, D.W. Ming<sup>2</sup>, J. L. Eigenbrode<sup>3</sup>, D. P. Glavin<sup>3</sup>, P. Mahaffy<sup>3</sup>, J. Stern<sup>3</sup>, R. Navarro-Gonzalez<sup>4</sup>, C. McKay<sup>5</sup>. <sup>1</sup>Jacobs-ESCG Houston TX 77058, <sup>2</sup>NASA Johnson Space Center, Houston TX 77058, <sup>3</sup>NASA Goddard Space Flight Center, Greenbelt, MD 20771, <sup>3</sup>Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, <sup>4</sup>NASA Ames Research Center, Moffett Field, CA 94035.

**Introduction:** The Sample Analysis at Mars (SAM) instrument detected four releases of carbon dioxide (CO<sub>2</sub>) that ranged from 100 to 700°C from the Rocknest eolian bedform material (Fig. 1). Candidate sources of CO<sub>2</sub> include adsorbed CO<sub>2</sub>, carbonate(s), combusted organics that are either derived from terrestrial contamination and/or of martian origin, occluded or trapped CO<sub>2</sub>, and other sources that have yet to be determined. The Phoenix Lander's Thermal Evolved Gas Analyzer (TEGA) detected two CO<sub>2</sub> releases (400-600, 700-840°C) [1,2]. The low temperature release was attributed to Fe- and/or Mg carbonates [1,2], perchlorate interactions with carbonates [3], nanophase carbonates [4] and/or combusted organics [1]. The high temperature CO<sub>2</sub> release was attributed to a calcium bearing carbonate [1,2]. No evidence of a high temperature CO<sub>2</sub> release similar to the Phoenix material was detected in the Rocknest materials by SAM. The objectives of this work are to evaluate the temperature and total contribution of each Rocknest CO<sub>2</sub> release and their possible sources.

**Materials/Methods:** The Rocknest eolian bedform material consists of unconsolidated sand and dusty material [5]. Four replicate Rocknest samples (< 150 µm) were heated in SAM at a rate of 35°C min<sup>-1</sup> from ambient to 840°C at a pressure of 30 mb with a He carrier gas flow rate of ~1.5 sccm. Evolved gases were analyzed by a quadrupole mass spectrometer (QMS) over the entire temperature range. The CO<sub>2</sub> release data was fitted with a Gaussian multi-peak fitting routine (IGOR Pro 6.2) to quantify the contribution of each CO<sub>2</sub> release to the total amount of CO<sub>2</sub>.

A laboratory Setaram Sensys-Evo differential scanning calorimeter coupled to a Stanford Research Systems Universal Gas Analyzer at NASA Johnson Space Center (JSC) have been configured to operate similar to the SAM oven/QMS system. This JSC-SAM-testbed is utilized to collect analog QMS data that can be used to interpret SAM-QMS data. The JSC SAM-testbed operates at 30 mb He with a 3 ml min<sup>-1</sup> flow rate. Calcite (Chihuahua, Mexico), magnesite (Winchester, WI) and siderite (Fe<sub>0.65</sub>Mg<sub>0.35</sub>CO<sub>3</sub>) (Copper Lake Nova Scotia, Canada) were evaluated for comparison to CO<sub>2</sub> release temperatures detected by the SAM-QMS on Mars

## Results/Discussion:

All four Rocknest soils had four releases of CO<sub>2</sub> with peaks at 225 (peak 1), 296 (peak 2), 398 (peak 3), and 488°C (peak 4). Using Rocknest 2 data, CO<sub>2</sub> release masses were ~ 0.01, 0.02, 0.04, and 0.03 wt% C, respectively [10.8 (±1.3) µmole total CO<sub>2</sub> released, 75 mm<sup>3</sup> sample volume [6] and assuming bulk soil density 1.7 g cm<sup>-3</sup> (Fig. 1)]. The calculated sample mass could change as sample delivery volume and bulk density continues to be investigated. All reported C concentrations are preliminary and are used to constrain the C-bearing phases in Rocknest.

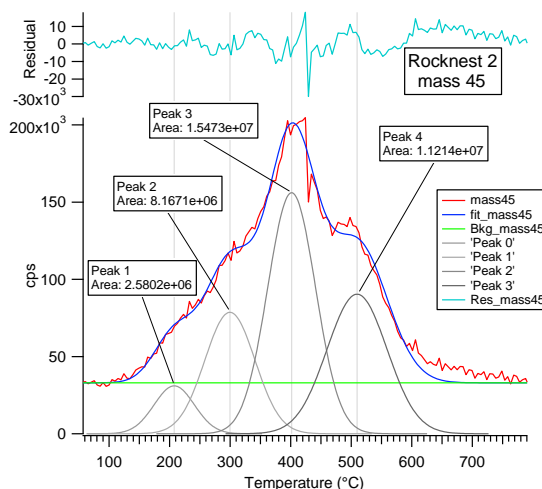


Fig. 1. Rocknest sample 2 CO<sub>2</sub> (mass 45) versus temperature (red). Grey peaks are Gaussian fits to the overall CO<sub>2</sub> release that sum to the blue line. Residual (light blue) is at top.

The lowest temperature peak could mostly be attributed physisorbed atmospheric CO<sub>2</sub>. Physisorbed constituents are held by intermolecular forces (van der Waal) and are typically released at temperatures below 200°C. The amount of CO<sub>2</sub> released (0.01 wt.% C) is also reasonable for a few monolayers of CO<sub>2</sub> adsorbed on Rocknest materials.

Peak 4 CO<sub>2</sub> release occurs at temperatures that are consistent with the thermal decomposition of siderite (Fig. 2). A siderite composition of Fe<sub>0.5</sub>Mg<sub>0.5</sub>CO<sub>3</sub>, suggests that at least 0.8 wt.% siderite may be present in the Rocknest material. CO<sub>2</sub> release from magnesite decomposition overlaps the peak 4 release but peaks at temperatures higher than siderite. Nevertheless, mag-

nesite is still being considered a possibility and more work is needed to verify its presence. Calcite (not shown) decomposition begins at 685°C which is where the Rocknest CO<sub>2</sub> releases are almost finished. This suggests that coarse grained calcite is not a likely candidate for Rocknest bedform material.

Peaks 2 and 3 and possibly some of peak 4 have CO<sub>2</sub> contributions from oxidation of organics that may be derived from the SAM instrument [7,8]. However current estimates of SAM derived organics suggest that only ~0.03 % of total C detected can be derived from SAM [7].

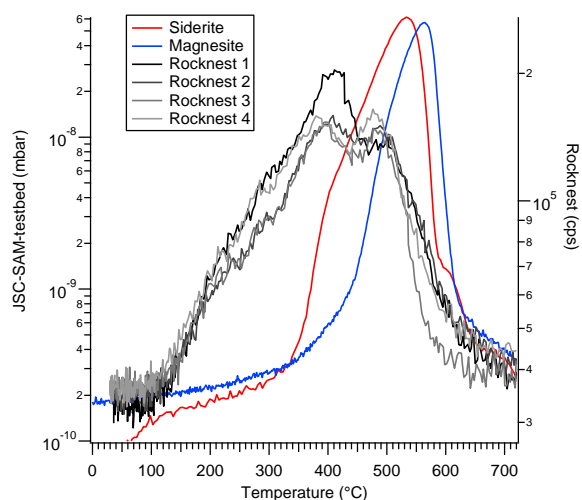


Fig. 2. Rocknest CO<sub>2</sub> releases (mass 45) versus temperature along with siderite and magnesite decomposition CO<sub>2</sub> releases as determined by the JSC-SAM-testbed.

Some of the C derived from peaks 2 and 3 could be derived from organic carbon in the Mars soil. Total C in Mars surface materials derived from meteoritic (CI) influx is estimated to be 0.03 to 0.10 wt.% C [9] which suggests that up to 0.05 wt.% C may occur as organic C in Mars surface material [e.g., 10]. The 0.025 wt.% C concentration is considered an upper limit for meteoritic derived organics and is likely lower due to Mars surface chemical processes that may oxidize surface organic carbon. This indicates that other sources of inorganic carbon likely exist to account for the 0.06 wt.% C in peaks 2 and 3.

Smaller particle sized carbonates are a potential source of the lower temperature CO<sub>2</sub> releases. Recent work [4,11] has demonstrated that calcite particle size has an effect on calcite decomposition temperatures. Calcite particles in the 2-50 µm range have a 20°C lower decomposition temperature than 250 µm size calcite particles. This temperature drop may not explain the ~90°C difference between peaks 3 and 4. However, proposed nanophase carbonates have been

shown to have at least a 100°C lower decomposition temperature relative to 2 to 50 µm sized calcite particles [4]. These results suggest that nanophase carbonates may explain part of the contribution to the peak 2 and 3 CO<sub>2</sub> releases.

Decomposition of other phases at peak 2 and 3 temperatures with carbonate may lower carbonate decomposition temperature in the Rocknest material. For example, hydrated Mg-perchlorate releases HCl upon decomposition and can partially decompose carbonate, releasing CO<sub>2</sub> at temperatures below normal carbonate decomposition temperatures [3]. While Mg-perchlorate is not the leading perchlorate candidate for Rocknest [12] the possibility exists that other phases yet to be evaluated may be promoting lower temperature decomposition of carbonate.

**Conclusions:** Four CO<sub>2</sub> releases from the Rocknest material were detected by SAM. Potential sources of CO<sub>2</sub> are adsorbed CO<sub>2</sub>, (peak 1) and Fe/Mg carbonates (peak 4). Only a fraction of peaks 2 and 3 (0.01 C wt.%) may be partially attributed to combustion of organic contamination. Meteoritic organics mixed in the Rocknest bedform could be present, but the peak 2 and 3 C concentration (~0.21 C wt. %) is likely too high to be attributed solely to meteoritic organic C. Other inorganic sources of C such as interactions of perchlorates and carbonates and sources yet to be identified will be evaluated to account for CO<sub>2</sub> released from the thermal decomposition of Rocknest material.

#### References:

- [1] Boynton et al. (2009) *Science*, 325, 61.
- [2] Sutter et al. (2012) *Icarus*, 218, 290.
- [3] Cannon et al. (2012) *GRL* 39, L13203.
- [4] Lauer et al. (2012) *LPS XLIII*, #2299.
- [5] Edgett et al. (2013) *LPS XLIV*.
- [6] Archer et al. (2013) *LPS XLIV*.
- [7] Glavin et al. (2013) *LPS XLIV*.
- [8] Eignebröde et al. (2013) *LPS XLIV*.
- [9] Yen et al. (2006) *JGR*, 111, E12S11.
- [10] Grady and Wright, (2003) *Space Sci. Rev.* 106, 231.
- [11] Archer P. D. Jr. et al. (2012) *Planet. Sci.*, submitted.
- [12] Sutter et al. (2013) *LPS XLIV*.